AD-A080 840 BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY F/G 11/2
COMPARATIVE RAMAN STUDY OF MIXED-ALKALI AND SIMILAR ION EXCHANG--ETC(U)
DEC 79 C WINDISCH, W M RISEN N00014-75-C-0883
UNCLASSIFIED TR-79-02 NL

1 OF 1
AD
A080840

END
DATE
FILMED
3-80
DDC

LEVEL IV

OFFICE OF NAVAL RESEARCH

Contract ONR-N00014-75-C-0883 NR-051-539

TECHNICAL REPORT NO. TR-79-02

(12)

ADA080840

Comparative Raman Study of Mixed-Alkali and Similar Ion Exchanged Glasses

by

Charles Windisch and William M. Risen, Jr.

Prepared for Publication

in the

Journal of Non-Crystalline Solids

December 10, 1979

DDC
RECEIVED
FEB 14 1980
E

DDC FILE COPY

Department of Chemistry
Brown University
Providence, RI 02912

December 10, 1979

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited.

80 2 14 007

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(14) **REPORT DOCUMENTATION PAGE**

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: TR-79-02

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) (6)
Comparative Raman Study of Mixed-Alkali and Similar Ion Exchanged Glasses

5. TYPE OF REPORT & PERIOD COVERED (9)
Technical Rept.

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) (10)
Charles Windisch ~~and~~ William M. Risen, Jr.

8. CONTRACT OR GRANT NUMBER(s) (15)
N00014-75-C-0883
NR-051-539

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Chemistry
Brown University
Providence, Rhode Island 02912

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS (11) 10
Office of Naval Research
United States Navy

12. REPORT DATE
Dec~~ember~~, 1979

13. NUMBER OF PAGES
36

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 39

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Distribution Unlimited; Approved for Public Release

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Ion-exchange, glass, mixed-alkali glass, ionic oxide glass, mechanical properties of glass, Raman spectra, ionic diffusion

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The Raman spectra of analogous ion exchanged and mixed alkali disilicate and aluminodisilicate glasses of the same relative composition of dissimilar cations have been determined and employed to investigate the origin of the similarity of the mechanical loss features exhibited by them. Ion exchange of Na^+ for Li^+ in Li_2O-Al_2O_3-$2SiO_2$ glasses is shown to yield glasses whose network structure is different from that of the mixed alkali glasses of the same stoichiometry, but to attain that structure upon annealing. The network structure of ion exchanged and conventionally mixed alkali disilicate glasses are apparently identical.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

405 436

Abstract (Contd)

These results are interpreted in light of the mechanical loss spectra of the analogous glasses prepared in the two ways.

Accession For
NTIS GRA&I ☑
DDC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or special
A

Comparative Raman Study of Mixed-Alkali and Similar Ion-Exchanged Glasses

Introduction

The fact that key dynamic mechanical properties of ion-exchanged glasses are strikingly similar to those of mixed-alkali glasses of approximately the same overall composition (1-6) has been reported by several investigators. In particular this similarity has been observed for each of the glass systems, $xLi_2O(1-x)Na_2O\cdot 2SiO_2$ (5) and $xLi_2O\cdot(1-x)Na_2O\cdot Al_2O_3\cdot 2SiO_2$ (6). Although evidence for it is clear, a well-developed rationale for this parallelism between the mechanical properties of conventionally "mixed alkali" and ion-exchanged glasses and experimental evidence on which to base such a rationale are lacking.

In the above-mentioned studies (5,6), the internal friction (tanδ) of mixed-alkali and analogous ion-exchanged glass fibers was determined as a function of temperature using the torsion pendulum technique at low frequency. Pertinent examples of these plots, shown in Figs. 1a through 2b, indicate the similarities. The so-called "mechanical mixed-alkali effect", as observed in the conventionally mixed alkali disilicates, is shown in Fig. 1a. As x is increased in this system ($xLi_2O\cdot(1-x)Na_2O\cdot 2SiO_2$) two effects are apparent. First, a lower temperature peak (LTP), sometimes called the "single-alkali" peak, shifts to higher temperatures and decreases in intensity; and, second, another peak, higher in temperature (HTP), often referred to as the "mixed-alkali peak", grows in and shifts to lower temperatures while increasing in intensity until x is near 0.5±.1. At approximately this composition the HTP is at its maximum and virtually obscures the LTP peak. As x is increased further, the HTP becomes weaker and shifts back to higher temperatures, while the LTP becomes again stronger and returns to lower temperatures. As shown in Fig. 1b, a similar "mixed-alkali" effect is observed in an ion-exchanged alkali disilicate glass. At this amount of Na for Li exchange the HTP is so intense that it nearly envelopes the LTP.

Figure 1

(a) Internal friction "Spectra" of conventionally melted $xLi_2O\cdot(1-x)Na_xO\cdot 2SiO_2$ (gl) glasses at (f = 0.5 Hz)

——·——· 0.06 Li_2O 0.94$Na_2O\cdot 2SiO_2$ (gl)
———— 0.5 $Li_2O\cdot 0.5Na_2O\cdot 2SiO_2$ (gl)
--------- 0.94 $Li_2O\cdot 0.06Na_2O\cdot 2SiO_2$ (gl) (5)

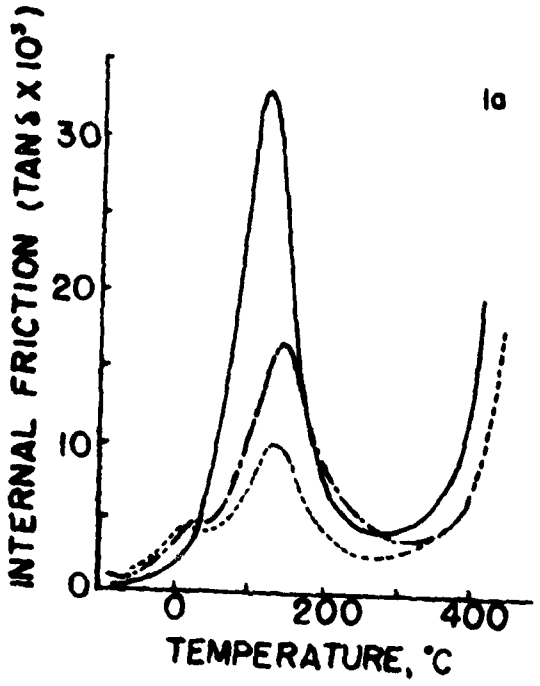
(b) Internal friction "Spectra" of $Na_2O\cdot 2SiO_2$ (gl) glasses before and after ion-exchange in $LiNO_3$, KNO_3, $NaNO_3$ mixture at 175°C. (f = 5 Hz)

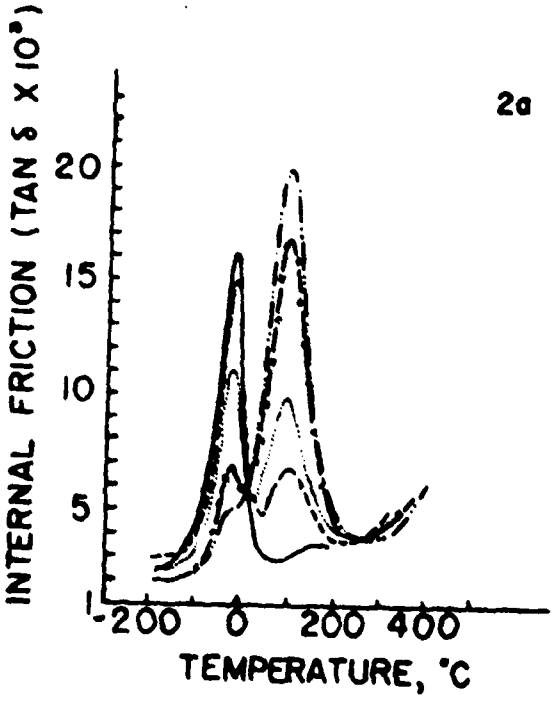
----- $Na_2O\cdot 2SiO_2$ (g)
——— $Na_2O\cdot 2SiO_2$ (g) after ion-exchange (½ hr) (5)

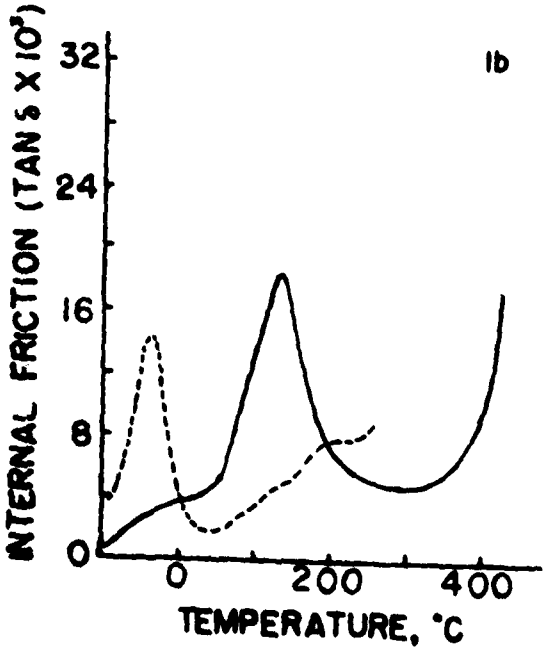
Figure 2

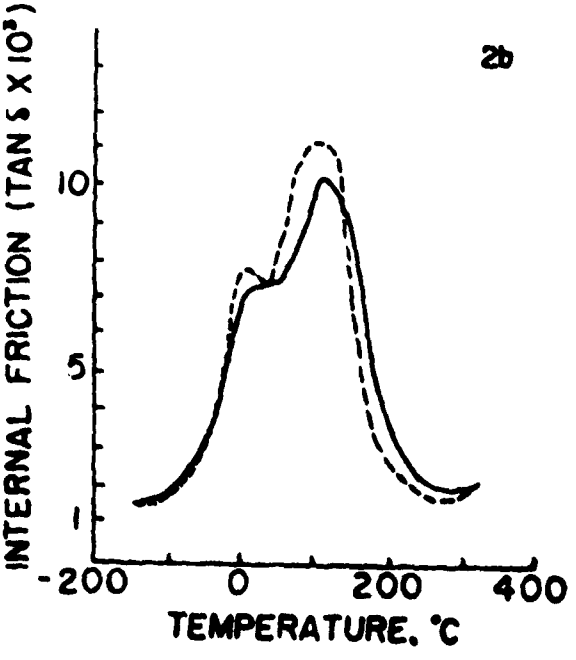
(a) Internal friction "Spectra" of $Li_2O\cdot Al_2O_3\cdot 2SiO_2$ (gl) ion-exchanged in $NaNO_3$ at 366°C (f = 0.5 Hz). —— 0 ---- 1; .... 5; —x— 30; ——··—60 minutes of exchange (6)

(b) Internal friction of $Li_2O\cdot Al_2O_3\cdot 2SiO_2$ (gl) ion-exchanged for 15 minutes in $NaNO_3$ at 366°C and a conventionally melted sample of the same composition (f = 0.6 Hz). —— ion-exchanged; --- conventionally melted: $0.9Li_2O\cdot 0.1Na_2O\cdot Al_2O_3\cdot 2SiO_2$ (6)


1a
INTERNAL FRICTION (TAN δ X 10³)
30
20
10
0
0
200
400
TEMPERATURE, °C


2a
INTERNAL FRICTION (TAN δ X 10³)
20
15
10
5
1
-200
0
200
400
TEMPERATURE, °C


1b
INTERNAL FRICTION (TAN δ X 10³)
32
24
16
8
0
0
200
400
TEMPERATURE, °C


2b
INTERNAL FRICTION (TAN δ X 10³)
10
5
1
-200
0
200
400
TEMPERATURE, °C

This phenomenon also is observed in ion-exchanged alkali alumino-disilicates, as can be seen in figure 2a. Again, the LTP becomes weaker as the HTP grows in and becomes quite strong at longer intervals of ion-exchange The similarity between an ion-exchanged glass and a conventionally mixed sample of identical composition, for the alkali alumino-disilicates, is shown in Fig. 2b.

The fact that an apparent "mixed-alkali" effect is observed in ion-exchanged glasses has caused speculation as to whether these glasses are indeed "mixed", i.e. have molecular level structures that are identical (or nearly identical) to those of compositionally identical but conventionally melted "mixed-alkali" glass systems. Although there are no convincing explanations for the origins of the effects observed, there have been suggestions about why certain phenomena are not observed. Thus, Abdel-Lalif, et al, attributed the failure of the HTP bands in ion-exchanged alumino-disilicates to shift in temperature to the lack of required network relaxation which is possible only at annealing temperatures (6). In the case of the alkali disilicates, de Waal, also emphasized the annealing process, and suggested that a mixed-alkali state is achievable after ion-exchange, if the glass structure is permitted to relax at an elevated temperature (5). In studies of certain other polysilicate systems (1-4, 7) similar conclusions have been reached. On the other hand, the presence of a mixed-alkali outer layer over a core of single-alkali silicate glass has been suggested as being the important characteristic in reaching a mixed-alkali-like state. Although it too must be valid under certain conditions, these conceptual approaches differ in the sequencing of the alkali diffusion-dispersion and network relaxation.

In order to address the question of whether the mixed alkali and ion exchanged glasses are as similar in structure as their mechanical properties have suggested, and of what the role of relaxation at annealing temperatures is, we have undertaken a study of the variation in molecular properties through analogous series of glasses. Our approach employs Laser-Raman spectroscopy to study these changes.

This method is based upon the assumption that if the structures found in ion-exchange and their analogous mixed-alkali glasses are the same, it should be apparent from the Raman spectra; and thus similarities in their mechanical spectra are to be expected. However, if the Raman spectra should differ significantly (due to microstructural variations or bulk heterogeneities, such as phase separation), then an explanation which is independent of these differences is required. In any event, a more profound explanation of the special mechanical behavior of mixed alkali glasses and ion-exchanged glasses is needed, and the spectra should assist in its formulation.

Experimental Procedure

Preparation of Mixed-Alkali Disilicates. Mixed-alkali glasses of the composition $xLi_2O\cdot(1-x)Na_2O\cdot 2SiO_2$ were prepared following the procedure used by de Waal (5) from appropriate amounts of reagent-grade SiO_2 (floated powder, 240 mesh), Na_2CO_3 and Li_2CO_3. After mechanically combining the components, about 7g of the mixture was melted in a 20 ml platinum crucible at 1350°C in an open air electric furnace. Enough time was given to allow the melts to become visibly homogeneous. Bubbles of CO_2 are liberated during the reaction and tend to linger within the viscous fluid melt. But with occasional stirring (with a fused silica rod) over the heating time of 3 to 4 hours, a clear melt of each composition in the series was obtained.

Upon removal from the furnace, the melts were allowed (about 15 seconds) to become viscous enough for fibers to be drawn. Glass fibers about 0.5 mm in diameter and 15 mm long were then drawn with a fused SiO_2 rod, cooled, broken into 5 cm lengths, and stored in a dessicator over $CaSO_4$.

Elemental analyses were performed on the mixed alkali disilicate fibers by Galbraith Labs, Inc., Knoxville, Tennessee. The actual alkali compositions of representative fibers (expt) compare with the melt compositions (predicted) as follows. For $0.85\ Li_2O\cdot 0.15\ Na_2O\cdot 2SiO_2$; Li(expt) 7.6% (pred.) 7.6%, Na(expt) 4.0% (pred.) 4.4%. For $0.5Li_2O\cdot 0.5Na_2O\cdot 2SiO_2$; Li(expt) 4.2% (pred.) 4.2%,

Na(expt) 13.8% (pred.) 15.3%. And, for $0.25Li_2O \cdot 0.75Na_2O \cdot 2SiO_2$; Li(expt) 2.0% (pred.) 2.0%, Na(expt) 19.8% (pred.) 19.7%. Thus, the actual compositions are quite close to the nominal ones for which the batches were prepared, and the experimental compositions are employed wherever relevant.

Preparation of Mixed-Alkali Aluminodisilicates. A similar procedure was followed in preparing mixed-glasses of the composition $xLi_2O \cdot (1-x)Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. Reagent-grade Al_2O_3 was used in addition to SiO_2 and the alkali carbonates. The mixtures were heated at 1550°C to obtain a homogeneous melt; and as for the previous system, glass fibers were drawn and stored in a dessicator.

Preparation of Ion-Exchanged Glasses. Glass fibers of $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ (x = 1) were used for the ion-exchange experiments. Following the procedure of Abdel-Latif, et al, (6) exactly, the fibers were cut to about 2 cm in length, immersed in a 20 ml crucible of molten $NaNO_3$ at 350°C for various amounts of time, and stirred periodically. After exchange, they were cooled, washed with distilled water, dried, and stored in a dessicator over $CaSO_4$. To confirm that exchange had occurred and to provide a connection between exchange time and total amount of exchange elemental analysis of an ion-exchanged fiber was carried out by Galbraith Labs. It showed that the Na^+ for Li^+ ion exchange that occurred in 24 hours under these conditions yielded a fiber whose ratio of Na^+ ions to Li^+ ions was 3.05 to 1.0. This corresponds in overal stoichiometry to $0.247\ Li_2O \cdot 0.753\ Na_2O \cdot 2SiO_2$.

The effect of annealing on the ion-exchanged alkali aluminodisilicates was also examined. Fibers of $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$(g) which had been Na-exchanged for 24 hours was heated at 590°C in an open-air electric furnace also for 24 hours, and their Raman spectra examined.

Raman Spectra. Raman spectra were obtained for all of the samples prepared using a Jarrell-Ash 25-300 Raman Spectrometer, and the 488.0 nm line of a Spectra Physics 164 Argon ion laser excitation. The fibers were oriented such that their cross sections were perpendicular to the excitation beam. Radiation scattered

at 90° was collected by the detector. The laser beam diameter was slightly greater than fiber thickness, so the spectra contain Raman Scattering from the entire fiber and any scattering elements present in the sample should contribute to the spectra.

Electron micrographs of both the alkali silicates and alkali aluminodisilicates were taken using an AMR Model 1000A Scanning Electron Microscope. Glass fibers were mounted such that their cross sections were exposed for analysis. These were polished and gold coated previous to microscope examination. At a magnification of 1000x the samples were homogeneous. Photographs at magnification 8000x show some irregularities attributable to tiny bubbles of CO_2 trapped within the glass or to stress cracks.

Spectral Results

Mixed Alkali Disilicate Spectra

The Raman Spectra of the glass system $xLi_2O\cdot(1-x)Na_2O\cdot 2SiO_2$ exhibit four prominent bands, each of which shifts in frequency as x changes. As shown in Figure 3a for x = 0, 0.5, and 1.0. The most notable shift occurs for the high frequency band, which occurs at approximately $1100cm^{-1}$. A summary of its behavior is presented in Fig. 5a. Changes are also observed in the broad band which occurs at approximately 575 cm^{-1}, and they are presented in Fig. 6a. The small shift in frequency of this band (about 10 cm^{-1}) probably is due to the effect of the change in background intensity that occurs as Li^+ is replaced by Na^+ in the mixed alkali series.

Sodium Ion-Exchanged $Li_2O\cdot 2SiO_2$ Fibers. Comparison of the bands in the Raman spectra ion-exchanged glasses with those of the conventional mixed alkali glasses shows their similarity quite clearly. The Raman spectra of $Li_2O\cdot 2SiO_2$(gl) ion-exchanged for various times in $NaNO_3$ (1) are shown in Fig. 3b. As is apparent from Fig. 5b the "1100 cm^{-1}" Raman band shifts in an identical fashion with increasing Na^+ content in both the mixed alkali and ion-exchanged glasses. After

Figure 3

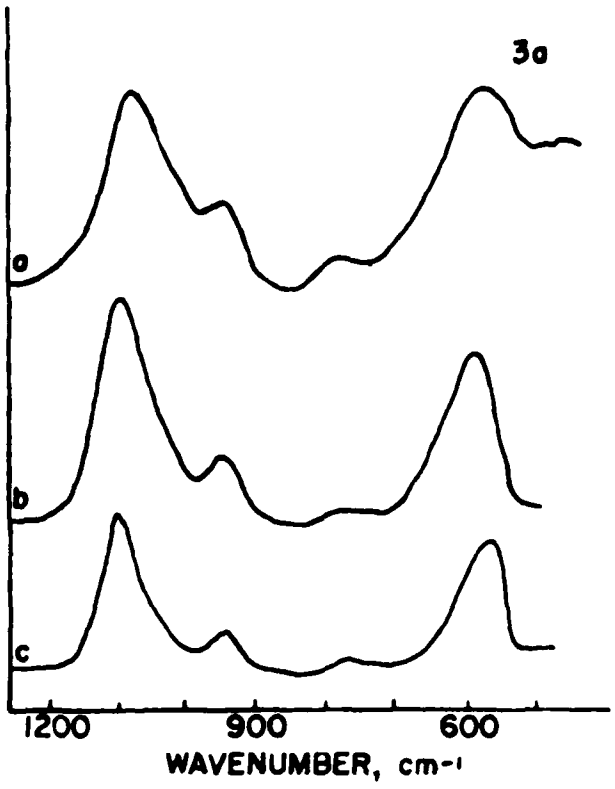
(a) Raman spectra of the $xLi_2O\cdot(1-x)Na_2O\cdot 2SiO_2$ (gl) System (a) x =1; (b) x = 0.5; (c) x = 0.

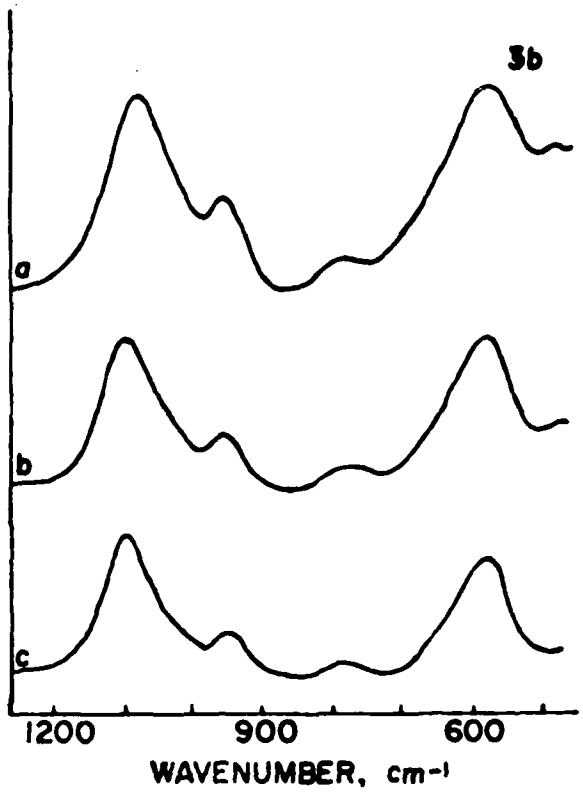
(b) Raman spectra of the $Li_2O\cdot 2SiO_2$ (gl) ion-exchanged in $NaNO_3$ at 350°C for various lengths of time: (a) 0 minutes; (b) 1 hr; (c) 2 hrs.

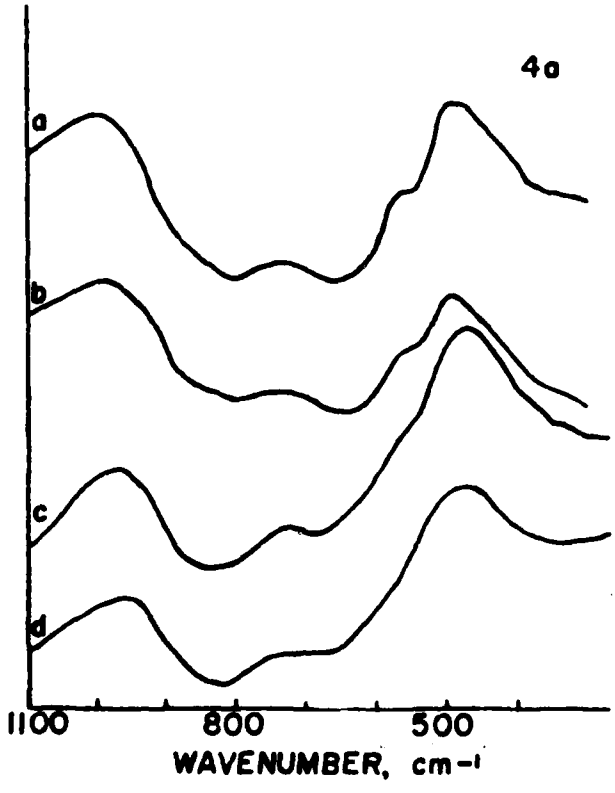
Figure 4

(a) Raman spectra of the $xLi_2O\cdot(1-x)Na_2O\cdot Al_2O_3\cdot 2SiO_2$ (gl) System; (a) x = 0.1; (b) x = 0.35; (c) x = 0.5; (d) x = 1.

(b) Raman spectra of the $Li_2O\cdot Al_2O_3\cdot 2SiO_2$ (gl) ion-exchanged in $NaNO_3$ at 350°C for various lengths of time (unannealed); (a) 24 hrs.; (b) 30 minutes; (c) 0 minutes.


3a
a
b
c
1200
900
600
WAVENUMBER, cm-1


3b
a
b
c
1200
900
600
WAVENUMBER, cm-1


4a
a
b
c
d
1100
800
500
WAVENUMBER, cm-1

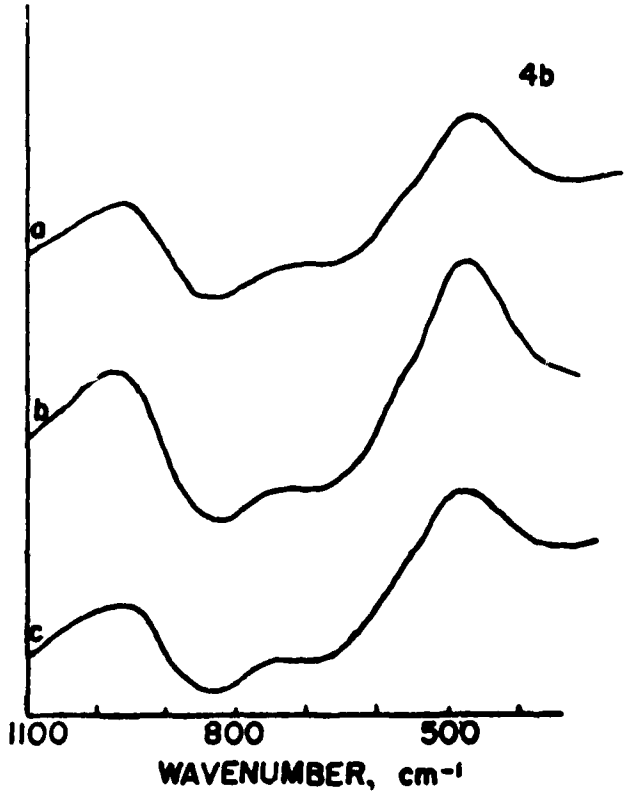
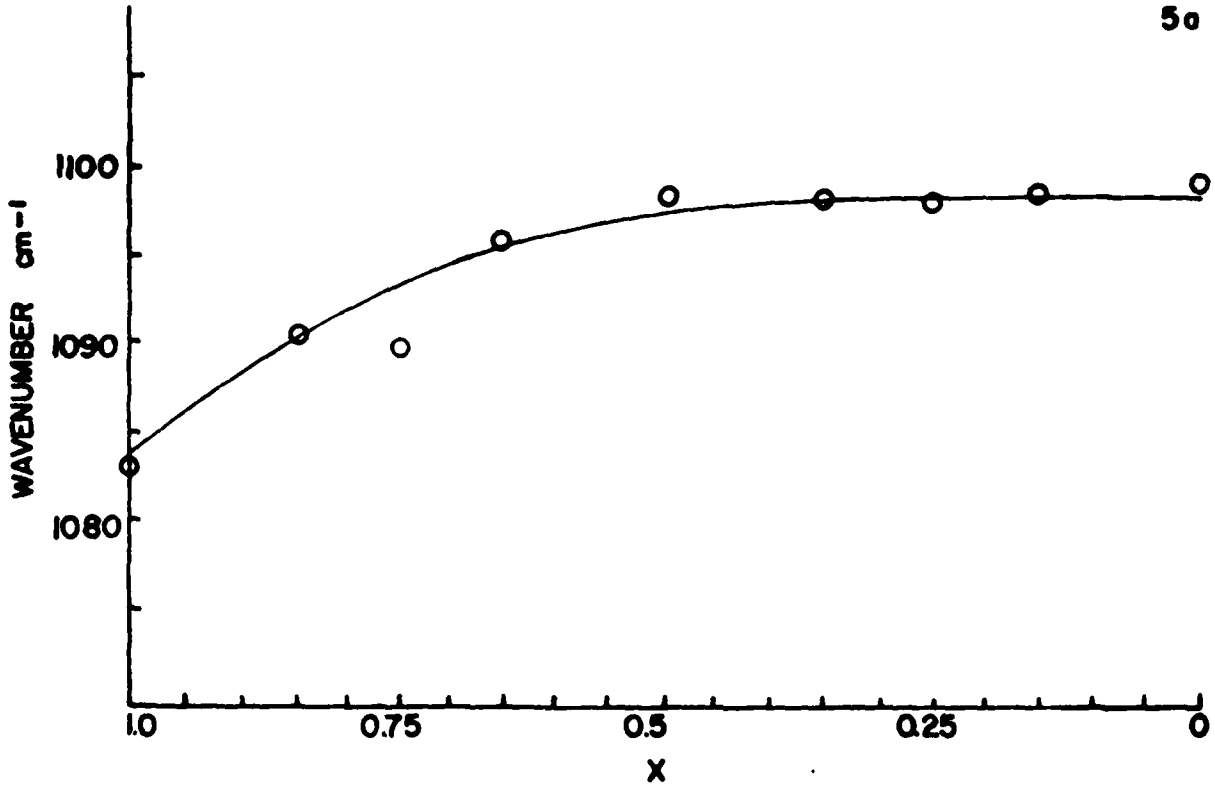

4b
a
b
c
1100
800
500
WAVENUMBER, cm-1

Figure 5

(a) Frequency of "1100 cm^{-1}" Raman band as a function of x for the system; $xLi_2O \cdot (1-x)Na_2O \cdot 2SiO_2$ (gl).

(b) Frequency of "1100 cm^{-1}" Raman band for $Li_2O \cdot 2SiO_2$ (gl) as a function of the time of ion-exchange in $NaNO_3$ at 350°C.


5a
1100
1090
1080
WAVENUMBER cm-1
1.0
0.75
0.5
0.25
0
X

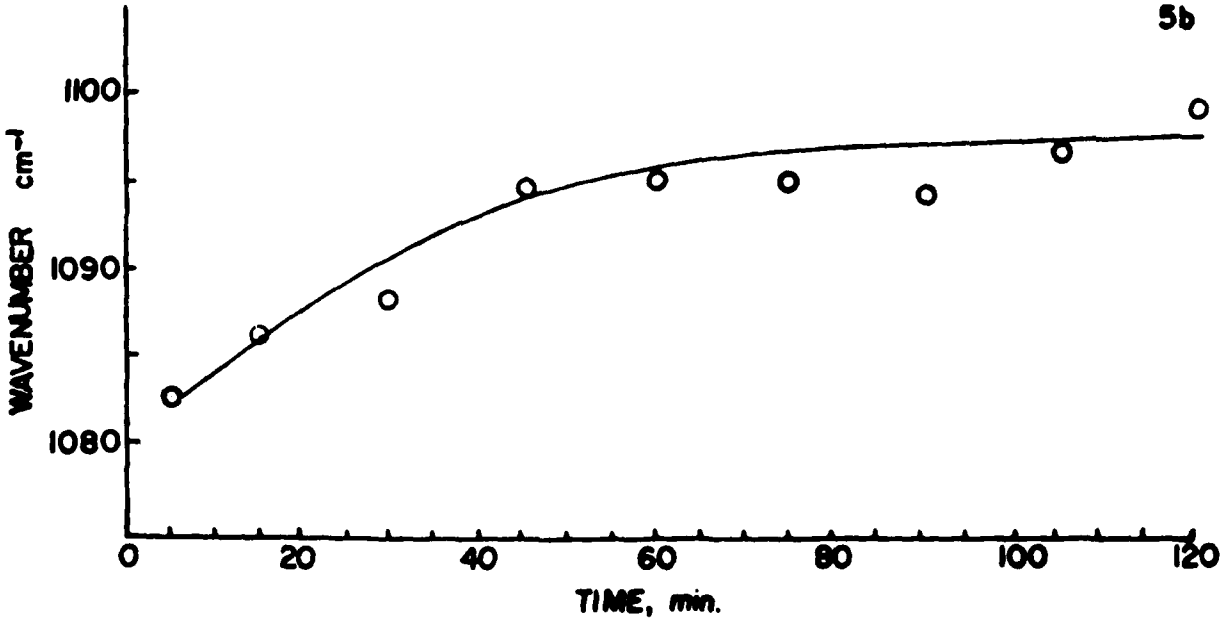
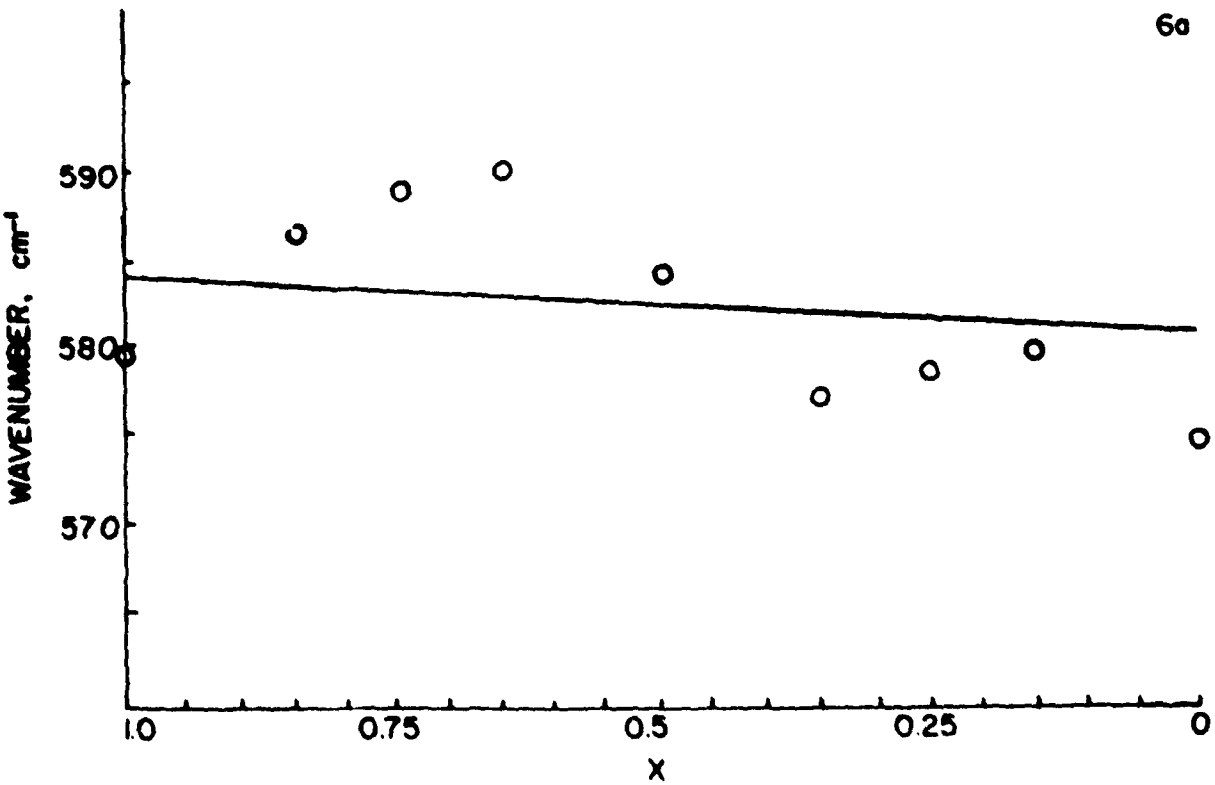
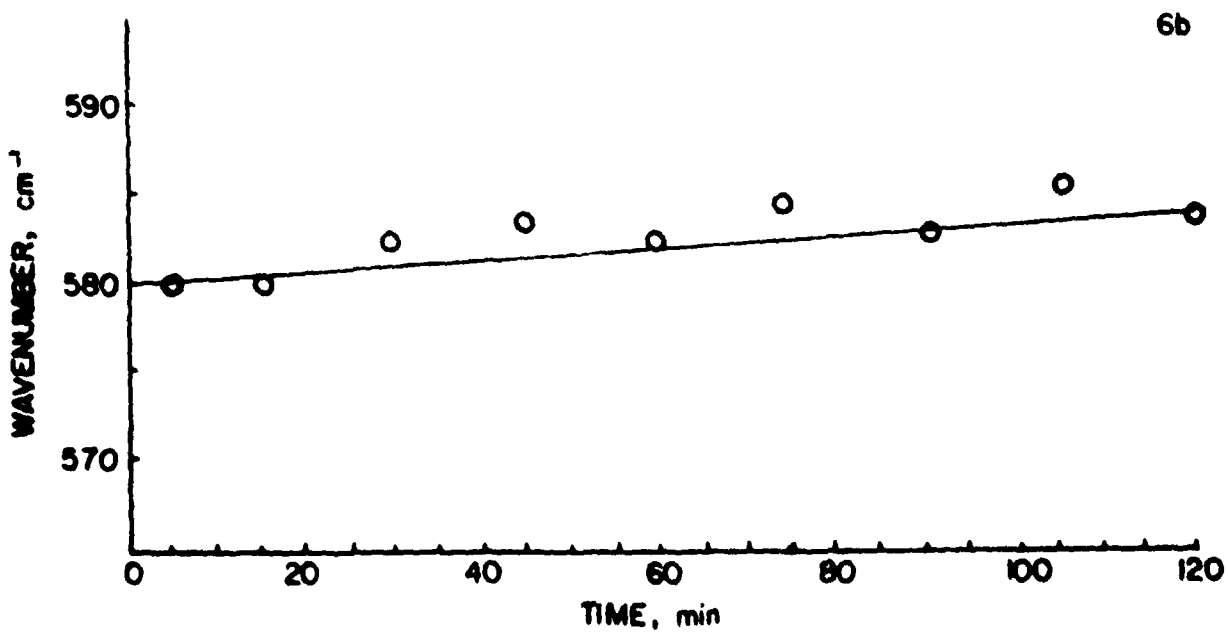

5b
1100
1090
1080
WAVENUMBER cm-1
0
20
40
60
80
100
120
TIME, min.

Figure 6

(a) Frequency of "575 cm^{-1}" Raman band as a function of x for the system; $xLi_2O \cdot (1-x)Na_2O \cdot 2SiO_2$ (gl)

(b) Frequency of "575 cm^{-1}" Raman band for $Li_2O \cdot 2SiO_2$ (gl) as a function of the time of ion-exchange in molten $NaNO_3$ at 350°C.


6a
590
580
570
WAVENUMBER, cm⁻¹
1.0
0.75
0.5
0.25
0
X


6b
590
580
570
WAVENUMBER, cm⁻¹
0
20
40
60
80
100
120
TIME, min

one to two hours, it appears that sufficient lithium has been replaced with sodium to cause a shift of this band to nearly the frequency it has in the single alkali glass $Na_2O \cdot 2SiO_2$. While the "575 cm^{-1}" band does not shift in a pronounced way that is separate from the changes in background scattering, similar changes in background are observed in the 500 cm^{-1} region. It is clear from these spectra that no significant modifications appear to occur to the network structure itself as one cation replaces the other in either the mixed and ion-exchanged alkali disilicate systems. Thus both systems are quite similar. As noted in the Discussion, if the disilicates alone had been studied, the role of network relaxation would not have been apparent, and the effects of ion exchange could be attributed to subtle changes in average cation-network distances and interaction forces.

Mixed-alkali Aluminodisilicates. The spectral behavior of the glass system $xLi_2O \cdot (1-x)Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, is quite different from that of the disilicates. As is seen in Fig. 4a, three bands stand out in these spectra; and, although these bands do not shift appreciably as x changes, two changes are quite evident.

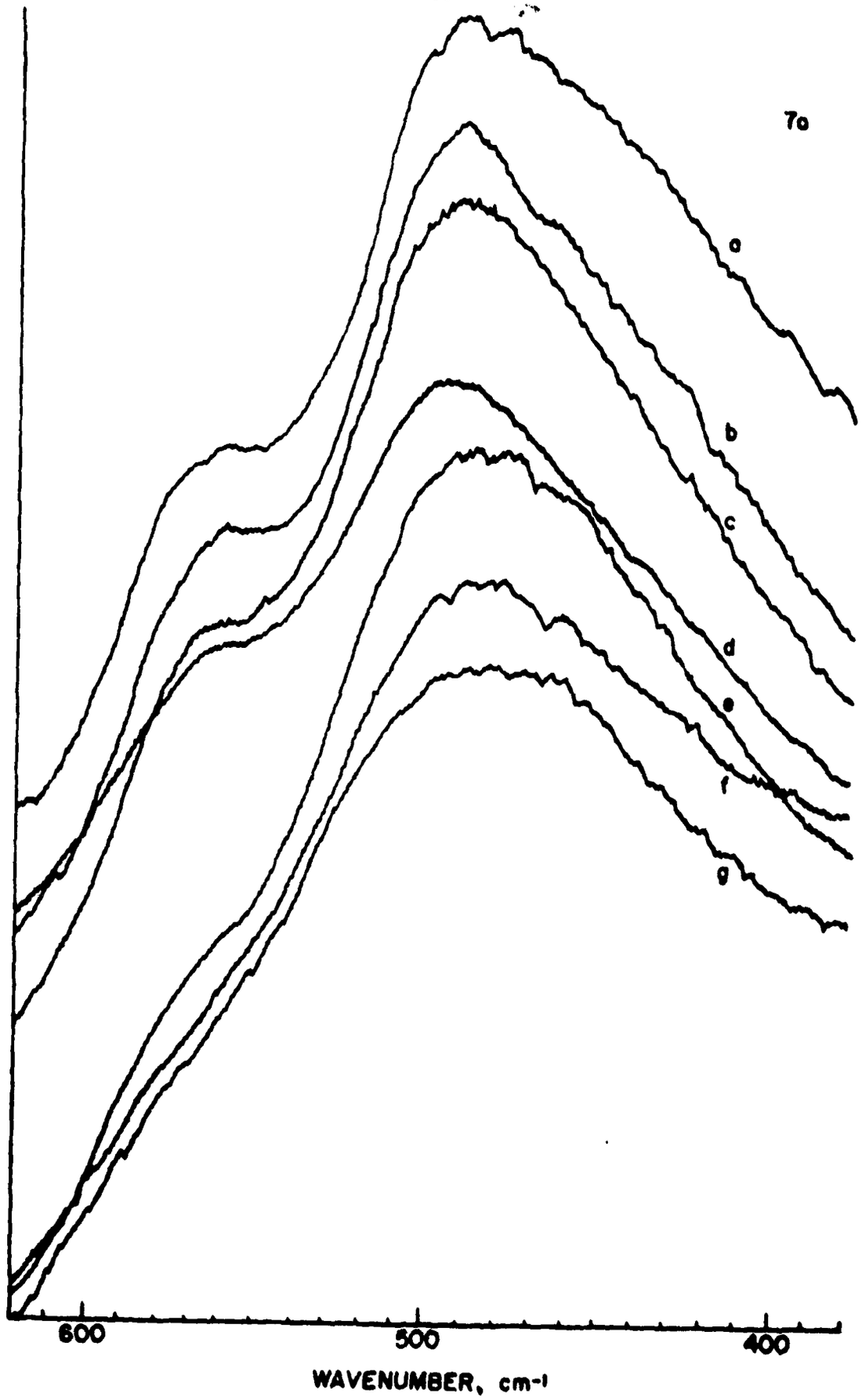
First, as x decreases, a new band appears at 560 cm^{-1}, as shown in Fig. 4a for x = 0.1, 0.5 and 1.0, and grows as more sodium is substituted for lithium in the glass system. Secondly, as x decreases, the band shape of the lower (492 cm^{-1}) band also changes, with the appearance of a broad lower frequency shoulder. Both of these effects are clearly seen in Fig. 7a. These "new" bands may have been present at low intensity, but concealed under the 500 cm^{-1} band, at high x.

Ion-Exchanged Alkali Aluminodisilicates. As is shown in Fig. 4b, spectral changes observed in the mixed-alkali aluminodisilicate spectra (the growth of the 560 cm^{-1} band and the alteration of shape of the 492 cm^{-1} peak) do not occur for the ion-exchanged glasses of the same composition. For, although there appears to be a hint of a band on the high frequency side of the 500 cm^{-1} peak, it does not change in magnitude with ion exchange for as long a period as

Figure 7

(a) The 400-600 cm^{-1} region of the Raman spectrum for the $xLi_2O\cdot(1-x)Na_2O\cdot 2SiO_2$ (gl) system; (a) x = 0.1; (b) x = 0.15; (c) x = 0.25; (d) x = 0.35; (e) x = 0.5; (f) x = 0.75; (g) x = 1.

(b) The 400-600 cm^{-1} region of the Raman Spectrum for the $Li_2O\cdot Al_2O_3\cdot 2SiO_2$ (gl) glasses ion-exchanged for various lenghts of time in $NaNO_3$ at 350°C; (a) 24 hrs; (b) 30 minutes; (c) 5 minutes; (d) 0 minutes.


7a
a
b
c
d
e
f
g
600
500
400
WAVENUMBER, cm-1

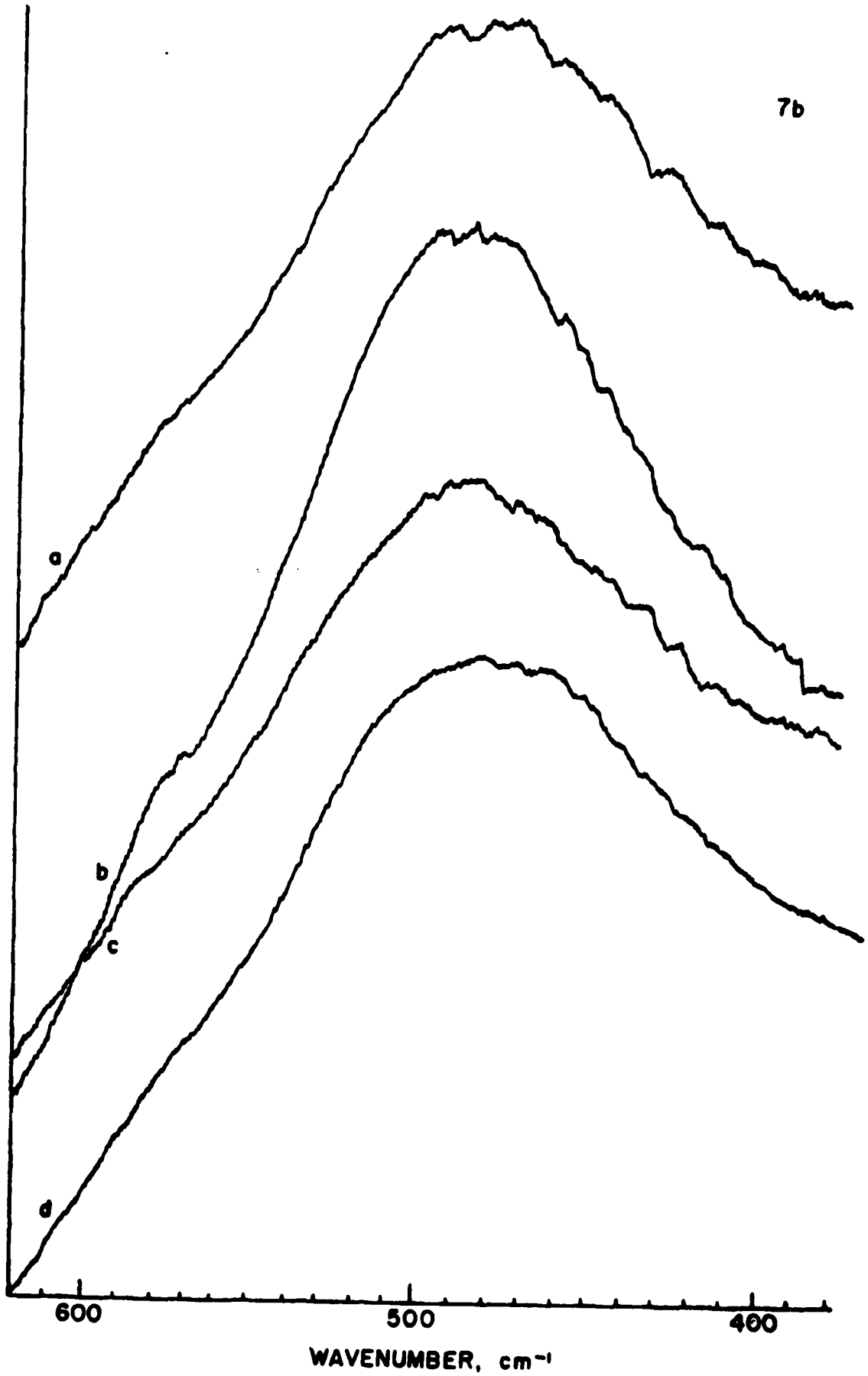
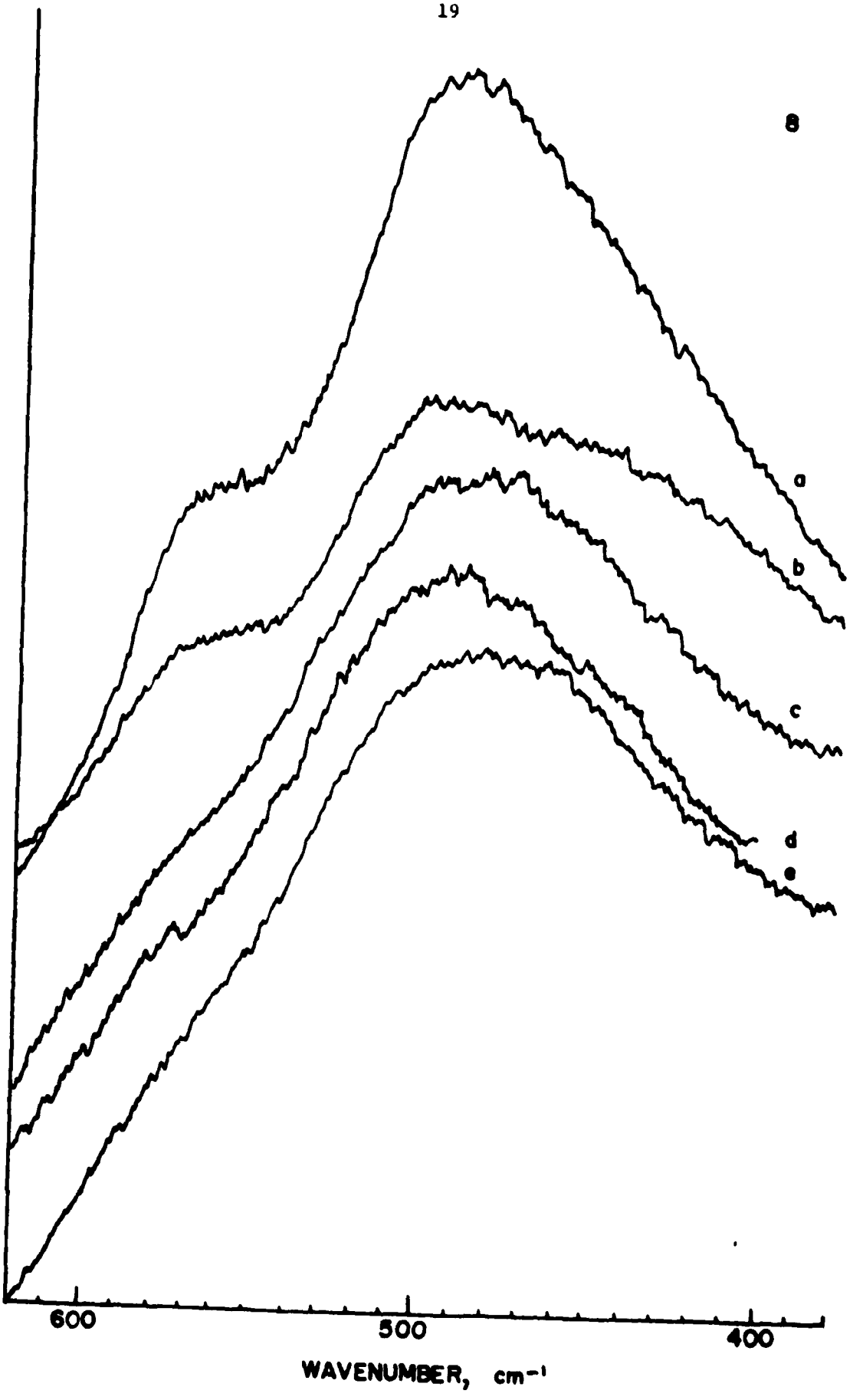

7b
a
b
c
d
600
500
400
WAVENUMBER, cm⁻¹

Figure 8

Raman spectra showing the effect of annealing a $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ (gl) fiber which had been exchanged in $NaNO_3$ at 350°C for 24 hours, by comparison with related glasses: (a) conventional mixed alkali glass of the composition $0.25Li_2O \cdot 0.75Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, (b) $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ (gl) fiber ion exchanged 24 hr and annealed 24 hr at 590°C; (c) same as (b) but without annealing, (d) $Li_2O \cdot Al_2O_3 \cdot 2SiO_3$ (gl) fiber annealed at 590°C for 24 hr; (e) same as (d) but without annealing.


8
a
b
c
d
e
600
500
400
WAVENUMBER, cm⁻¹

24 hours.

However, when an ion exchanged fiber is annealed at 590°C for 24 hr., its Raman spectrum develops these characteristics. As can be seen from Fig. 8, an annealed fiber of a glass ion-exchanged for 24 hrs (Fig. 8b) shows the growth of the 560 cm^{-1} band and a shape-change of the broad 492 cm^{-1} maximum. Its similarity to a mixed system can also be seen by comparing Figures 8a and 8b. While they do not have exactly the same shapes, they both show that a structural transformation leading to the appearance of the 560 cm^{-1} band occurs when the network organizes or reorganizes in the presence of both Na^+ and Li^+.

Spectral Assignments

In order to analyze the effects of the ion-exchange and the mixing processes on the bonding structures of the glasses, it is necessary to assign the Raman spectral features. Although no Raman studies of these or closely related mixed systems have been reported, the spectra of a variety of silicate glasses, including the end-number $Li_2O \cdot 2SiO_2$ and $Na_2O \cdot 2SiO_2$ (8-18), have been published (8,10,11,14). A number of assignments have been suggested for features commonly observed in silicate glasses and they help in identifying certain of the bands shown in Figures 3 and 4, despite the fact that there are clear conflicts between the published assignments.

On the basis of the stoichiometry and crystal structures of $Li_2O \cdot 2SiO_2$ and $Na_2O \cdot 2SiO_2$ (gl), it is known that the silicon atoms are tetrahedrally bound to oxygens and that three of the oxygens per silicon bridge to another silicon. A "chain" structure is found for the crystals. The glassey state is disordered over the long range, but the local structures may be taken to be similar. The disorder of the glass introduces a large number of perturbations on the vibrations, and they contribute to the breadth of the spectral bands, but the general features of the spectrum are attributable to reasonably well separated

vibrational modes. Thus, modes due to terminal Si-O stretching motions, in-chain Si-O-Si stretches, Si-O-Si and O-Si-O bending motions are observed. Although they are coupled, sufficient separation exists in the frequency regime to permit making assignments.

The assignment of the major features of the spectra of $M_2O \cdot 2SiO_2$(gl) materials is given in Table I. The 1100 cm^{-1} and 945 cm^{-1} bands are due to motions which must be coupled. Although these assignments are consistent with the work of Ferraro (16) and the discussion of Hass (9), they differ from those of Konjnendijk and Stevels (13) in major respects,which include the assignments of the 945 cm^{-1} and 1100 cm^{-1} bands. They suggest that the appearance of a ca 950 cm^{-1} band in a silicate glass is due to a structure containing two non-bridging oxygens on a silicon atom, and that this is consistent with assigning the 1100 cm^{-1} band to the vibration of a structure with one non-bridging oxygen. While that is self consistent, it does not account for the Si-O stretches in the chain and it is inconsistent with our observation that a band analogous to the 1100 cm^{-1} band is observed (1004 cm^{-1}) in alumino silicate glasses having structures with no non-bridging oxygens at all.

The spectral changes observed upon substitution of Na^+ for Li^+ in the $M_2O \cdot 2SiO_2$ glass system are relatively small and are consistent with small changes in the cation-polyanion force field. As shown in our earlier studies (19,20), this results in small changes in both the strengths and angles of the network bands.

The assignments of the Raman bands in the $M_2O \cdot Al_2O_3 \cdot 2SiO_2$(gl) series are somewhat less straightforward because the spectrum obtained in any given case depends on the preparative conditions. In particular, the 560 cm^{-1} band appears in the spectra of the conventional mixed alkali alumino disilicates

Table I

Assignments of Principal Raman Bands in the 400-1200 cm^{-1} Region for $M_2O \cdot 2SiO_2$ and $M_2O \cdot Al_2O_3 \cdot 2SiO_2$ Glasses

A. $M_2O \cdot 2SiO_2$ Glasses

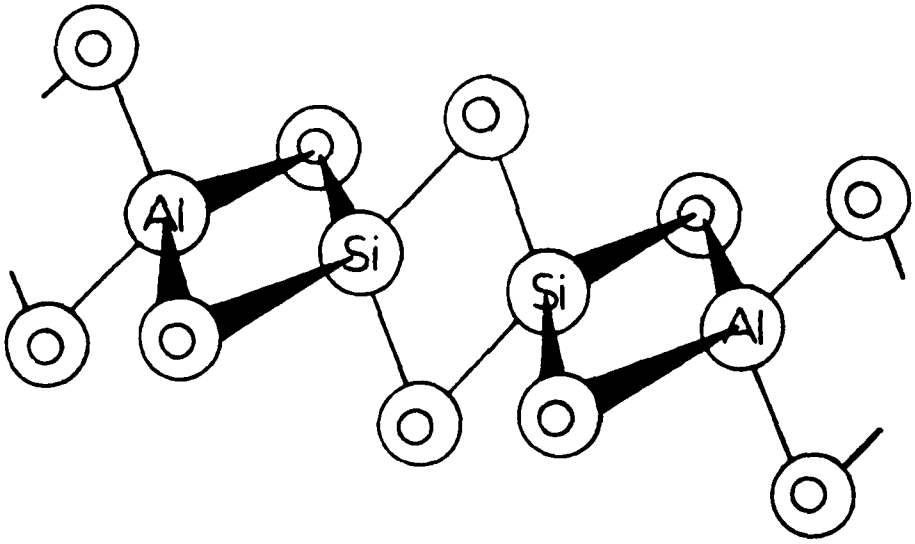
$Na_2O \cdot 2SiO_2$(gl)	$Li_2O \cdot 2SiO_2$(gl)	Assignment
1100 cm^{-1} (vs)	1083* cm^{-1} (vs)	ν(Si-O-Si) stretch
945	949	$\nu(Si\text{-}O_t^-)$ stretch
770	780	δ(O-Si-O) bend
575* (vs)	580 (vs)	δ(Si-O-Si) bend

B. $M_2O \cdot Al_2O_3 \cdot 2SiO_2$(gl)

$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$(gl) (14)	0.9 $Na_2O \cdot 0 \cdot 1L_2O \cdot Al_2O_3 \cdot 2SiO_2$	
1004 cm^{-1} (vs)	1005 cm^{-1} (vs)	ν(Si-O-Si)+ν(Si-O-Al) +ν(Al-O-Al)
736	735	δ(O-Si-O)+δ(O-Al-O)
568	560	δ(Si-O-Si)+δ(Si-O-Al) +δ(Al-O-Al) in new structure (see Fig. 10)
468	492 (vs)	δ(Si-O-Si)+δ(Al-O-Al) +δ(Si-O-Al) in chain structure.

* This band was reported at 565 cm^{-1}, ref (10).

9



as the Na^+-content increases and in the spectra of annealed Na^+-exchanged lithium alumino-disilicate glasses. But, it does not appear in unannealed glasses at any level of exchange. It is associated with a structural feature that is not present in the pure Li^+-containing glass or any unannealed Na^+-exchanged glass.

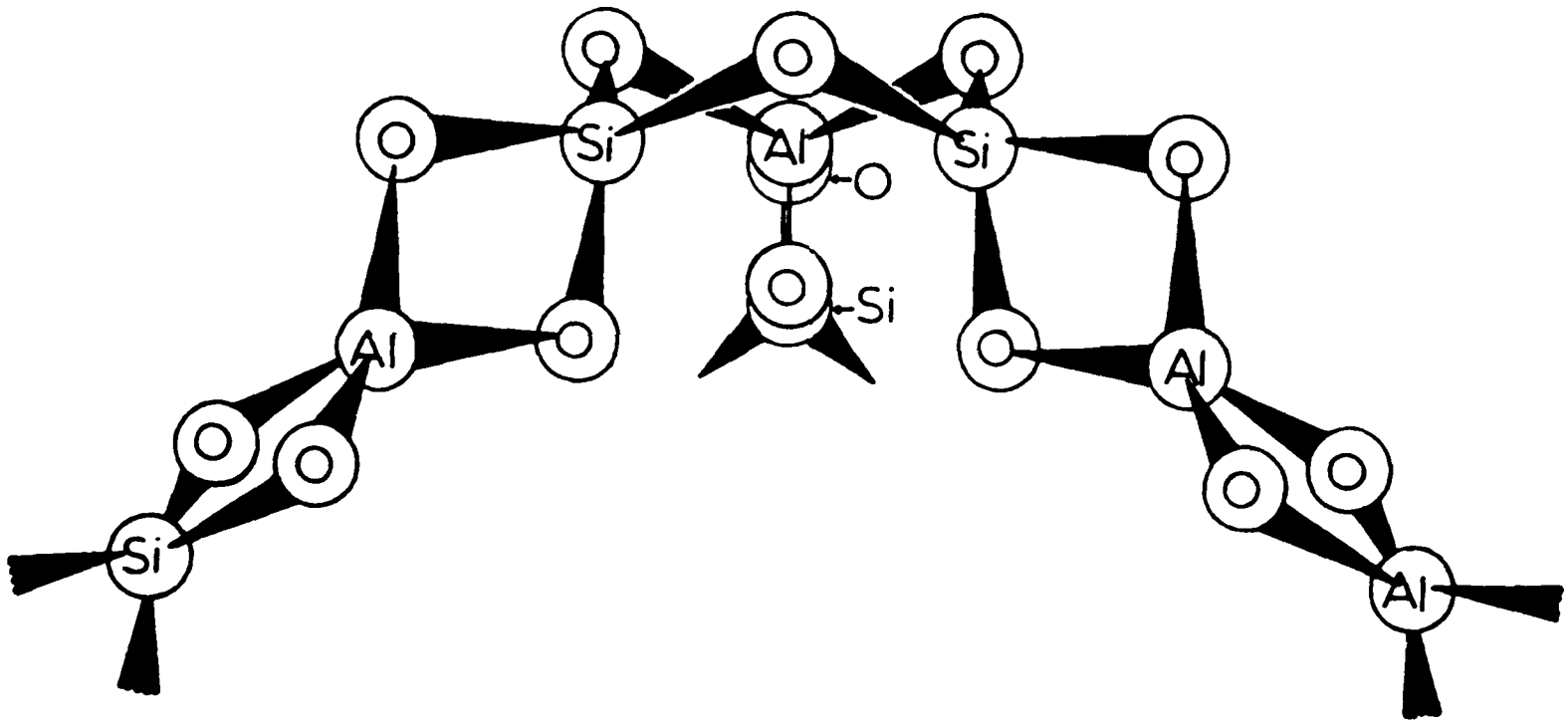
From the stoichiometry of $M_2O \cdot Al_2O_3 \cdot 2SiO_2$ it is evident that all oxygens must be involved in bridging, if it is assumed that both Si and Al are tetrahedrally bound and there are no defects. There must be some defects, of course, but it should be noted that introducing six coordinate Al (a commonly proposed kind of defect) does not free oxygens to become terminal rather than briding. Thus, the principal features of the spectra of the alumino disilicates are attributed to vibrations of structures involving only bridging oxygens.

The ca 1005 cm^{-1} band is clearly due to the symmetric stretch of the A-O-B units (where A and B are Si or Al) and the lower frequency modes are due to bending. The 560 cm^{-1} band which grows into the spectrum is assigned to deformations of a new structural grouping which satisfies the stoichiometry and has similar tetrahedrally coordinated Al and Si atoms with bridging oxygens. This grouping, however, has the characteristic that it is more probable when the larger (Na^+) cation is present and that it is more rigid and thus has a higher deformation frequency. As discussed below, this could be the ring-type chain junction shown in Figure 10. The 560 cm^{-1} band would then be assigned to deformations of the A-O-B angles of this structure.

Discussion

The spectral results on the disilicate and aluminodisilicate glass systems are strikingly different and provide new insight into the relationship between the ionic diffusion and network relaxation (or rearrangement) processes

10



and the roles they play in glass formation and modification. By analyzing these results it is possible to see that in the aluminodisilicate case the processes can be separated to a considerable extent, but in the disilicates they cannot.

In both the lithium and sodium disilicate glasses, the network structures are apparently about as similar as they are in the crystalline forms of these materials. Thus, whether a given ratio of Na^+ to Li^+ content is achieved by ion exchange or by conventional melt mixing to form mixed alkali glasses, nearly the same network results. The major change accompanying the ion exchange process in this case is simply diffusion of the ions. Naturally small changes in average cation-network separation, cation-cation interactions, and other interactions must also accompany the process, but the Raman spectra indicate that they do not cause significant network modifications. Therefore, the ion exchanged glasses in which the ions have distributed themselves randomly can be thought of as having mechanical properties that are similar to those of the mixed alkali glasses for the simplest of reasons; they are very similar glasses.

In the case of ion exchanged disilicate glasses in which the ions do not have sufficient time to distribute themselves as randomly as possible, it is clear that a cation concentration gradient exists and decreases in exchange-ion concentration from the surface into the bulk. They may have mechanical behavior ranging from that of a perturbed pure single alkali glass to that of a composite material. Since the network spectral features are not very different for the Na^+ and Li^+ forms of the disilicates, such gradients do not show up in the spectra even though the spectral sampling method exposes the entire sample cross section. The far infrared spectrum of ground, ion-exchanged glasses

show that the cation motion vibrations are similar to those in the single alkali glasses.

The fact that the ion-exchanged and conventionally mixed alkali disilicates are spectroscopically similar does make it possible to assert that their mechanical properties should be similar, and, specifically, that a "mixed alkali peak" or MTP should appear in the ($\tan\delta$ vs x) mechanical loss spectrum. However, it does not directly provide an understanding of the origin of this feature, and it does not address the question of whether network relaxation is necessary to make the two forms of glass of the same overall composition closely similar.

On the other hand, the study of the aluminodisilicate glasses provides more insight into the nature of the processes involved.

The process of making a mixed alkali glass by ion exchange that is equivalent to one that is made by conventional melting can be divided conceptually into the cation exchange (diffusion) process and the network relaxation process. The first can lead to a spatial distribution of cations throughout the bulk that is about the same in glasses prepared either way. The second can lead to a network structure in an exchanged glass that is equivalent to the one achieved in the mixed alkali melt. Although these processes are never completely separable, a significant separation of them was achieved in these experiments.

As discussed above, the spectra of $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$(gl) fibers that are about 75% exchanged with Na^+ do not show the 560 cm^{-1} Raman band that appears in the spectra of mixed alkali aluminodisilicate glasses of the same composition. Since exchange at this level assures extensive (though non-uniform) distribution of Na^+ ions throughout the sample, it is clear that the 560 cm^{-1} band would appear in the spectrum if it were due simply to the presence of Na^+ at sites

in the unaltered network. Thus, mixing the alkali ions does not cause the glass to achieve a state equivalent to that of the conventionally melted mixed alkali glass.

However, it does cause the appearance of a mechanical loss peak (HTP) similar to the one observed for the mixed alkali glass (Fig. 2b). This clearly means that the presence of a distribution of dissimilar cations is associated with the HTP peak regardless of whether the network has reached the state it has after either melting or annealing. It does not mean that the motion of this collection of dissimilar cations is, in fact, the process that causes the mechanical loss, but only that their presence is an essential feature. Nor does it mean that their presence explains the (HTP) mechanical loss, because such a loss peak for an ion exchanged glass does not always vary with composition (i.e. T_p vs x) in the way it does for a conventional mixed alkali glass.

Thus, we may conclude so far from these data that the presence of a distribution of dissimilar cations, however attained, satisfies a necessary condition for a (HTP) mechanical loss peak but does not fully explain it. Were it to be both a necessary and sufficient condition it would also explain its variation with x.

When an ion-exchanged (at 75% Na^+, for example) aluminodisilicate glass is annealed at 590°C for 24 hr, the 560 cm^{-1} band appears. The network rearrangement accomplished by this annealing results in formation of the structures favored by the presence of Na^+. The similarity of the Raman spectrum of the ion exchanged glasses (8_b) to that of the melted mixed alkali glass (8a) indicates that the Na^+ ions assist in the rearrangement which yields such structures. As depicted in Fig. 10, the formation of chain junctions leads to ring structures that are more open and provide an energetically and sterically more favorable position for the Na^+ than does the tighter chain structure

apparently favored by the smaller Li^+ ion. A reasonable low energy path to achieve this structure can be constructed in which the Na^+ assists in the postulated bond rearrangements.

In previous work the 560 cm^{-1} band in aluminosilicates was attributed to defects in the glass networks (15), producing Si and Al atoms attached to one or more non-bridging oxygens. Acknowledging the presence of a small number of such defects, since the stoichiometry requires that all oxygens in the network be bridging, the proposed new structural feature seems most reasonable. The effect such a ring formation would have on the spectrum would have to be calculated to be evaluated with certainty, but it is quite likely that it would include the appearance of two new bending modes in the 500 cm^{-1} region. The more constrained angles of the ring (B) are expected to make one such deformation appear at a frequency higher than the 490 cm^{-1} band, and we have assigned the 560 cm^{-1} band to that mode.The α angles may be more easily deformable and give rise to the increased scattering intensity below 490 cm^{-1}.

From these experiments on the aluminodisilicates, then, we conclude that the ion exchange leads to a distribution of dissimilar cations and an accompanying rise of a mechanical loss peak (HTP) which is similar to that of a mixed alkali glass, but that it arises without a network structural change. At higher temperatures, achieved by annealing or melting, a network structural change occurs separately. This rearrangement or relaxation resulting from annealing is a change toward the structure formed in and quenched from the melt of the same composition. The rates of the ionic diffusion and network change are sufficiently different and their spectral effects are different enough that the kinetics of the two processes can be studied seaparately.

Although the presence of dissimilar cations is essential to the appearance

of the HTP, the HTP involves network rearrangements. Moreover, the segment of the network whose relaxation gives rise to the HTP must vary with composition for T_p of the HTP to vary. Thus, we can postulate that a network rearrangement becomes probable and gives rise to a mechanical loss peak when a large number of equivalent configurations is available to the system; i.e., when its configurational entropy increases. However, the temperature dependence of the peak is a function of both the nature of the network and the size of the rearranging segment required to sample enough points in the configuration space for the rearrangement to become probable.

Acknowledgment

This work was supported in part by the Office of Naval Research. This support is gratefully acknowledged.

References

1. W. E. Steinkamp, J. E. Shelby, and Delbert E. Day, "Internal Friction of Mixed-Alkali Silicate Glasses," J. Amer. Ceram. Soc., 50 (5), 271 (1967).
2. T. D. Taylor and G. E. Rindone, "Internal Friction of Ion-Exchanged Glasses," ibid., 51 (5), 289-90 (1968).
3. T. D. Taylor and G. E. Rindone, "Reply by T. D. Taylor and G. E. Rindone" (to reference (4)), ibid., 53 (4), 227 (1970).
4. James E. Shelby, Jr., "Mechanical Relaxation of Ion-Exchanged Alkali Silicate Glasses," ibid., 53 (4), 226 (1970).
5. H. deWaal, "Internal Friction of Sodium Disilicate Glass After Ion-Exchange," Phys. Chem. Glasses, 10 (3), 108-16 (1969).
6. A. Ismail, A. Abdel-Latif and Delbert E. Day, "Internal Friction of Ion-Exchanged $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ Glass," J. Amer. Ceram. Soc., 55 (6), 279-84 (1972).
7. James E. Shelby, Jr., and Delbert E. Day, "Mechanical Relaxations in Mixed-Alkali Silicate Glasses I, Results", J. Am. Ceram. Soc., 52 (4), 169-174 (1969).
8. Jean Etchepare, "No. 126-Sur L'Interpretation des Spectres de Diffusion Raman Raman de la Silice Vitreuse et de Verres Binaires de Silicates Alcalins," J. Chem. Phys., 67, 890-94 (1970).
9. Marvin Hass, "Raman Sepctra of Vitreous Silica, Germania and Sodium Silicate Glass," J. Phys. Chem. Solids, 31, 415-22 (1970).
10. Steven Brawer, "Theory of the Vibrational Spectra of Some Network and Molecular Glasses," Phys. Rev. B, 11 (8), 3173-94 (1975).
11. Steven A. Brawer and William B. White, "Raman Spectroscopic Investigation of the Structure of Silicate Glasses. I. The Binary Alkali Silicates," J. Chem. Phys., 63 (6), 2421-32 (1975).
12. William Leendert Konijnendijk, "Structural Differences between Borosilicate and Aluminosilicate Glasses Studied by Raman Scattering," Glastechn. Ber., 48, 216-18 (1975).

13. W. L. Konijnendyk and J. M. Stevels, "Raman Scattering Measurements of Silicate Glasses and Compounds," J. Non-Crys. Solids, 21 (3), 447-53 (1976).

14. Steven A. Brawer and William B. White, "Raman Spectroscopic Investigation of the Structure of Silicate Glasses (II). Soda-Alkaline Earth-Alumina Ternary and Quaternary Glasses," J. Non-Crys. Solids, 23, 261-78 (1977).

15. S. K. Sharma, D. Virgo, and B. Mysen, Annual Report of the Director, Geophysical Laboratory, 2801 Upton Street, Northwest, Washington, DC 20008, 1977-1978; (Reprinted from) Carnegie Institution of Washington Year Book 77, 1977-1978, pp 649-62.

16. J. R. Ferraro and M. H. Manghnari, J. Appl. Phys., 43, 4595 (1972).

17. J. Wong and C. A. Angell, Glass Structure by Spectroscopy, New York and Basel: Marcel Dekker, Inc. (1976) p. 134.

18. Von Friedrich Liebau, Acta Cryst. 14, 389-406 (1961).

19. Arnis U. Paeglis, Spectroscopic Investigation of Structure and Glass Transition Behavior in Alkali Arsenate, Phosphate, and Arsenatophosphate Glasses, Ph.D. Thesis, Department of Chemistry, Brown University, 1979.

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1
ONR Branch Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106	1
ONR Branch Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Dr. Fred Saalfeld Chemistry Division Naval Research Laboratory Washington, D.C. 20375	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	
Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	
Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	
Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	
Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	
Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	
Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

472:GAN:716:abc
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Dr. Stephen H. Carr Department of Materials Science Northwestern University Evanston, Illinois 60201	1
Dr. M. Broadhurst Bulk Properties Section National Bureau of Standards U.S. Department of Commerce Washington, D.C. 20234	2
Dr. T. A. Litovitz Department of Physics Catholic University of America Washington, D.C. 20017	1
Professor G. Whitesides Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Professor J. Wang Department of Chemistry University of Utah Salt Lake City, Utah 84112	1
Dr. V. Stannett Department of Chemical Engineering North Carolina State University Raleigh, North Carolina 27607	1
Dr. D. R. Uhlmann Department of Metallurgy and Material Science Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Naval Surface Weapons Center White Oak Silver Spring, Maryland 20910 Attn: Dr. J. M. Augl Dr. B. Hartman	1
Dr. G. Goodman Globe Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Picatinny Arsenal SMUPA-FR-M-D Dover, New Jersey 07801 Attn: A. M. Anzalone Building 3401	1
Dr. J. K. Gillham Princeton University Department of Chemistry Princeton, New Jersey 08540	1
Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library Cl 290/36-84 AUTO-Sutton	
Dr. E. Baer Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. K. D. Pae Department of Mechanics and Materials Science Rutgers University New Brunswick, New Jersey 08903	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serofini, MS-49-1	1
Dr. Charles H. Sherman, Code TD 121 Naval Underwater Systems Center New London, Connecticut	1
Dr. William Risen Department of Chemistry Brown University Providence, Rhode Island 02192	1
Dr. Alan Gent Department of Physics University of Akron Akron, Ohio 44304	1

472:GAN:716
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, 356A

	No. Copies
Mr. Robert W. Jones Advanced Projects Manager Hughes Aircraft Company Mail Station D 132 Culver City, California 90230	1
Dr. C. Giori IIT Research Institute 10 West 35 Street Chicago, Illinois 60616	1
Dr. M. Litt Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	1
Dr. R. S. Roe Department of of Materials Science and Metallurgical Engineering University of Cincinnati Cincinnati, Ohio 45221	1
Dr. Robert E. Cohen Chemical Engineering Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. David Roylance Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02039	1
Dr. T. P. Conlon, Jr., Code 3622 Sandia Laboratories Sandia Corporation Albuquerque, New Mexico	1
Dr. Martin Kaufmann, Head Materials Research Branch, Code 4542 Naval Weapons Center China Lake, California 93555	1
Professor S. Senturia Department of Electrical Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1
Dr. T. J. Reinhart, Jr., Chief Composite and Fibrous Materials Branch Nonmetallic Materials Division Department of the Air Force Air Force Materials Laboratory (AFSC) Wright-Patterson Air Force Base, Ohio	4
Dr. J. Lando Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	
Dr. J. White Chemical and Metallurgical Engineering University of Tennessee Knoxville, Tennessee 37916	
Dr. J. A. Manson Materials Research Center Lehigh University Bethlehem, Pennsylvania 18015	
Dr. R. F. Helmreich Contract RD&E Dow Chemical Co. Midland, Michigan 48640	
Dr. R. S. Porter University of Massachusetts Department of Polymer Science and Engineering Amherst, Massachusetts 01002	
Professor Garth Wilkes Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, Virginia 24061	
Dr. Kurt Baum Fluorochem Inc. 6233 North Irwindale Avenue Azuza, California 91702	
Professor C. S. Paik Sung Department of Materials Sciences and Engineering Room 8-109 Massachusetts Institute of Technology Cambridge, Massachusetts 02139	